

# Electrocatalytic Activity of Core-shell Carbon-metal Nanocomposites Derived From Carbon Dioxide

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## ABSTRACT

The polymer electrolyte fuel cell (PEFC) is one of promising devices to convert chemical energy of fuels to electrical energy with high energy efficiency, high power density, and low environment impact. Despite wide applications in many areas, the large-scale commercialization of PEFCs is difficult because of the high cost of platinum-based electrocatalysts for oxygen reduction reaction (ORR) at cathode. There have been numerous efforts to developing alternative materials to platinum-based electrocatalysts and here we introduce boron-doped carbon/iron nanocomposites (Fe/B/C) as oxygen reduction electrocatalysts. They were synthesized through the reduction of CO<sub>2</sub> by NaBH<sub>4</sub> with a Fe precursor at 500 °C and atmospheric pressure. Furthermore we performed heat treatments of the resulting Fe/B/C at 850 °C, 1050 °C (sample named as FeBC050, FeBC850 and FeBC105). Fe/B/C composites have a core@shell structure, in which the iron-containing nanoparticles are confined within onion-like graphitic carbon shells. Electrochemical analyses in cyclic voltammetry (CV) and rotating disk electrode (RDE) showed Fe/B/C composites enhanced ORR activity and especially FeBC105 presented excellent performance. Through XRD analyses, XPS, SEM and HRTEM observations, the thermal annealing is proved to be the reason for this better performance that changes the surface state and more active sites are generated by both the reduction of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and the decomposition of B<sub>4</sub>C species.

**Keywords:** oxygen reduction reaction (ORR), B-doped, electrocatalyst, CO<sub>2</sub> conversion, core-shell nanocomposites

## 1 INTRODUCTION

A fuel cell is a device to convert chemical energy of fuels to electrical energy. Among many types of fuel cells, polymer electrolyte fuel cells (PEFCs) have demonstrated one of promising devices because of its many advantages such as high energy efficiency, high power density, low environment impact [1]. However it is difficult to commercialize because of the expensive platinum-based electrocatalyst for oxygen reduction reaction (ORR) at cathode [2-5]. Therefore, developing cost-effective ORR catalysts is required for the sustainable development of fuel cells. There have been many attempts to replace platinum-

based electrocatalyst with other efficient, low-cost electrodes. Iron (Fe), a non-precious metal catalyst, attested and showed the high electrocatalytic performance originating from the metal cations coordinated by nitrogen atoms of aromatic rings. These are incorporated into graphitized carbon matrices.

Heteroatom-doped such as nitrogen (N) [3,6,7-10] and boron (B) [11-14] can enhance the electrocatalytic activity of carbon-based materials toward ORR. Here, we introduce boron(B)-doped carbon/iron nanocomposites (Fe/B/C) as efficient ORR electrocatalysts because the electrocatalytic evaluation by introducing the Fe/B/C composite have never been explored.

## 2 EXPERIMENTAL SECTION

### 2.1 Synthesis of B-doped carbon/iron composites and characterization

The synthesis method of boron-doped carbon/iron composites are composed of three steps. The first step is Fe precursor synthesis. The second step is preparation of boron-doped carbon/iron composites. The final step is a thermal annealing step. By adding 50 cm<sup>3</sup> sodium carbonate solution slowly to 50 cm<sup>3</sup> FeCl<sub>2</sub> solution in a glass beaker, Fe precursor is synthesized. When the particles precipitate, the supernatant was decanted, and then 150 cm<sup>3</sup> D.I. water was added. These steps were repeated ten times. Finally, the suspension was filtered and dried in oven at ca. 120 °C. The main crystalline phase of Fe precursor is magnetite (Fe<sub>3</sub>O<sub>4</sub>, PDF #19-0629) and goethite (FeOOH, PDF #29-0713) which is identified from the XRD spectrum. The reduction of CO<sub>2</sub> by NaBH<sub>4</sub> with the Fe precursor at 500 °C and atmospheric pressure forms the B-doped carbon/iron composites. DI water washing can leach salts from the solid product. Sequentially, the resulted Fe/B/C composite is annealed at 850 °C and 1050 °C in argon atmosphere.

To identify physical and chemical characteristics of Fe/B/C composites, we carried out powder X-ray diffraction (XRD) measurements, Raman spectra, X-ray photoelectron spectroscopy (XPS), high resolution transmission electron microscope (TEM) images and scanning electron microscope (SEM) images.

## 2.2 Electrochemical measurements.

Cyclic voltammetry (CV) and linear sweeping voltammetry (LSV) were performed at room temperature on a RRDE-3A rotating ring disk electrode rotator. The Ag/AgCl is a reference electrode and the platinum wire is served as a counter electrode. The glassy carbon (GC) rotating disk electrode was used as a working electrode. The inks deposited on the disk were made by mixing 5.0 mg catalyst and 1.0 mL solutions of water, methanol, and Nafion® with a volume ratio of 3:1:0.1 by ultrasonication for 10 min. About 7.5  $\mu\text{L}$  of the catalyst ink was loaded onto the polished carbon disk electrode for CV measurements.

## 3 RESULTS AND DISCUSSION

Cyclic voltammetry (CV) was employed to evaluate the electrocatalytic performance of the Fe/B/C composites and Pt (20 wt.)/carbon. In the case of Pt/carbon in an alkaline solution (1 M NaOH) saturated with 1 atm argon (Ar), oxide formation/reduction peaks and  $\text{H}_2$  adsorption/desorption peaks exist [15, 16]. FeBC050 is featureless at 0 to -1.2 V, whereas redox peaks of FeBC085 and FeBC105 in CV curve reveal well-defined at -1.2 to -0.4 V and become sharp along with the annealing temperature increase. In the  $\text{O}_2$ -saturated solution, cathodic peak and onset potentials decrease in the order of Pt/carbon, FeBC105, FeBC085, and FeBC050. For the comparison purpose, the peak potential of boron-doped carbon nanotubes is more negative than -0.31 V [6]. These show that thermal annealing enhances drastically the ORR activity of the Fe/B/C composites. We conducted the linear sweep voltammetric (LSV) measurements on a rotating disk electrode (RDE) in order to further analyze the ORR activity of the Fe/B/C composites. The LSV curves of FeBC105 is the same as those of Pt/carbon in terms of the limiting current.

Through the X-ray diffraction (XRD), the crystalline form of irons restricted within the B-doped carbons can be identified. The analysis showed that the main crystalline phase of FeBC050 is maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ). As the treatment temperature increases to 850  $^\circ\text{C}$ , maghemite is reduced to iron. After the heat treatment at 1050  $^\circ\text{C}$ , the carbide phase ( $\text{Fe}_x\text{C}$ ) occurs. Thus, the thermal treatment affects both the property of iron compounds and the nature of solid carbon. Also, Raman spectra support these changes. The D band shifts from 1370 to 1350  $\text{cm}^{-1}$  and becomes sharp after annealing at 850 and 1050  $^\circ\text{C}$ . This result is due to incorporating heteroatoms into the carbon network. It breaks its hexagonal symmetry and induces an increased D band in the Raman spectrum. After the heat treatment, 2D band becomes a pronounced peak in the spectra because of occurrence of metastable crystalline carbon.

From X-ray photoelectron spectroscopy (XPS), the chemical composition and bonding state of elements of a solid surface can be detected. For the FeBC050, the B 1s spectrum exhibits two envelopes. The first envelope is fitted by two peaks and these are respectively corresponding to B atoms bound to B atoms and B atoms connected to C carbons in  $\text{B}_4\text{C}$  species [17]. The other envelope is only fitted by one peak, corresponding to  $\text{BCO}_2$  species. The C 1s envelop consists of three peaks which are respectively matched with  $sp^2$ -hybridized carbon, defective carbon, and  $>\text{C}=\text{O}$  or C-O [18,19]. The O1s spectral envelop can be deconvoluted into three peaks which are assigned to Fe-O, C=O, and C-O species, respectively [18-20]. The characteristic signal of  $\text{BCO}_2$  species was not identified, possibly because of its low surface concentration. The Fe 2p spectrum has two envelopes, one for Fe  $2p_{3/2}$  and the other for Fe  $2p_{1/2}$  and a satellite peak for Fe  $2p_{3/2}$ . Fe  $2p_{3/2}$  which has four states is fitted by multiplets and a high binding energy (BE) surface peak. But Fe  $2p_{1/2}$  has only two, so it is deconvoluted into two peaks.

After heat treatment at 1050  $^\circ\text{C}$  (FeBC105), the most interest thing is that the B 1s spectrum has only one high BE envelope; these two peaks are assigned to  $\text{BC}_x\text{O}_y$  species. Also, which has high BE envelope occurs only for FeBC085. The C 1s spectral envelop consists of three peaks and these are respectively assigned to  $sp^2$ -hybridized carbon, defective carbon, and  $-\text{COO}$ . After annealing at 1050  $^\circ\text{C}$ , the relative concentration of defective carbon decreases which is corresponding to the appearance of metastable crystalline carbon in the XRD spectra. The O 1s spectral envelop is fitted by three peaks matched with Fe-O, C=O, and C-O species, respectively. For FeBC105, two new peaks appear; the former is ascribed to the metallic iron and the latter is possibly related to iron carbides. All of XPS and XRD observations demonstrate that  $\text{B}_4\text{C}$  species disappear, a decrease of defects in the carbon structure and a reduction of iron oxide to iron after the thermal annealing.

By scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM), its effect on the microstructure of the composite is discovered. As the thermal annealing increases, the porosity of boron-doped carbon/iron composites also amplifies. Sodium borohydride reacts with  $\text{CO}_2$  after melting to produce carbon which deposits on the solid iron precursor, resulting in a core-shell structure. HRTEM images show this specific structure. It looks like a onion because iron-containing nanoparticles are encapsulated into well-defined graphitic carbon shells. Its interplanar distance is ca. 0.34 nm, corresponding to the d-spacing of the (002) basal planes in graphite. In case of FeBC050, the interplanar distance of cores is about 0.24 nm which close to the d-spacing of the (311) planes in  $\gamma\text{-Fe}_2\text{O}_3$ . For FeBC105, the interplanar distance of cores is around 0.19 nm, approximating to the d-spacing of the (110) planes in  $\alpha\text{-Fe}$ .

The average electron transfer number is 1.96 at the range from -0.2 to -0.4 V but it increases up to 4.7 between -0.5 and -0.8 V. It indicates that oxygen reduction goes on by a two-electron pathway at negative potentials and a four-electron ORR reaction at more negative potential than -0.7 V. In proportion to the increase of the potential, the oxygen reduction mechanism changes accordingly.

In addition, FeBC105 shows an excellent tolerance of methanol crossover, which is another main challenge faced by metal-based cathode catalysts in fuel cells. In the absence of methanol, the current maintains of FeBC105 is around 0.17 and that of Pt/carbon is about 0.29 mA. When 1 cm<sup>3</sup> methanol added to 80 cm<sup>3</sup> electrolyte solution, the current of FeBC105 remains around 0.17 mA, but the current of Pt/carbon changes to -0.37 mA, and then only increases back to 0.03 mA. These results indicate that the annealed B-doped carbon/iron composites have excellent activity as electrocatalyst for ORR, high tolerance to the crossover effect, and relatively a small generation of peroxide.

#### 4 CONCLUSION

We have introduced a synthesis method of boron-doped carbon/iron composites from CO<sub>2</sub> at 500 °C and 1 atm. The synthesized composite has a core-shell structure composed of the iron-containing nanoparticles and the surrounding graphitic carbon shells. When the higher temperature is applied for the heat treatment, the electrocatalytic activity toward ORR in NaOH solutions enhanced. In addition to the improved catalytic activity, the high tolerance of methanol crossover and long-term stability of the heat treated composite were identified. The surface state change affects on the ORR performance. Tuning the microstructure of graphitic carbon shells increases the surface area to contact oxygen and thus, a direct 4-electron pathway could become favorable.

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